

Extraction coefficient:

- It indicates how much of the metal will move from the aqueous phase to the organic phase in a single contact

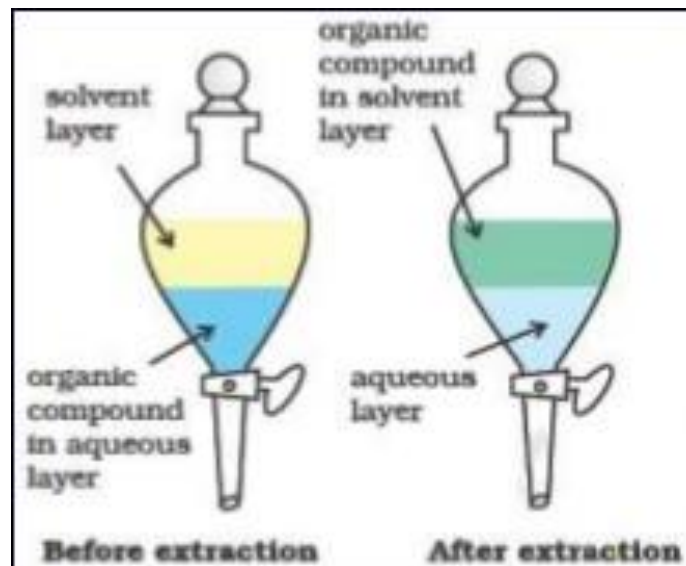
Effective extraction coefficient(E_F)

$$E_F = \frac{[M^{n+}]_{\text{org}} (\text{Vol.})_{\text{org}}}{[M^{n+}]_{\text{aq}} (\text{Vol.})_{\text{aq}}}$$

Single stage vs. Multistage

❖ Single Stage Solvent extraction

- Single stage process is commonly followed in laboratory scale
- Contacting is carried out by taking two phases together in a separating funnel followed by vigorous shaking so that the phase may disperse in each other as fine droplets. Ceasing the agitation lead to the separation of phases in two distinct layers



Single Stage Solvent Extraction:

From mass balance it can shown that

$$\frac{X_0}{X_1} = 1 + \frac{[M^{n+}]_{org} (Vol.)_{org}}{[M^{n+}]_{aq} (Vol.)_{aq}}$$

Where,

X_0 =Concentration of metal ions in the feed solution i.e the aqueous phase before any contact.

X_1 = Cocentration of metal ions in the aq. Raffinate i.e. the aq phase after a single contact



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❖ Multi Stage Counter Current Solvent Extraction

- For extraction of metals on industrial scale, multi stage counter current solvent extraction process is followed.
- The aqueous raffinate from one extraction unit is fed to the next unit as the aqueous feed, while the organic solvent flows in the opposite direction, thereby picking up more metal ions in successive contacts.
- Dividing the organic phase into small parts and making multiple contacts is the most efficient way of extracting

For a single contact:

$$\frac{X_0}{X_1} = 1 + E_F$$

For multistage contacts (assuming n contacts)

$$\frac{X_0}{X_n} = (1 + E_F/n)^n$$

As $\lim n \rightarrow \alpha$

$$\frac{X_n}{X_0} = \frac{1}{\exp(E_F)} = \exp(-E_F)$$

When separation factor, α is large, separation is easy, requiring little input of work. Thus, if α lies between 100 and 1,000, a single equilibration in liquid-liquid extraction is sufficient to separate at the level of 90 percent or higher. This type of process is called a **single-stage process**.

If the separation factor is smaller, separation is more difficult: more work must be done on the system to achieve the desired separation. This result can be accomplished by repeating the equilibration process many times, such a method being called a **multistage process**.

So, multistage contact is best

Solvent extraction and radiochemical analysis

- The heaviest elements need to chemically separate the nuclide(s) of interest from other radioactive species that are present. This is done by performing radiochemical separations that involve the conventional separation techniques of analytical chemistry
- Modern procedures sometimes are similar to qualitative analysis schemes, breaking products into chemically similar groups and using instrumentation to further separate the group members.
- Separation by liquid-liquid extraction (solvent-extraction) has played an important role in radiochemical separations. Ether extraction of uranium was used in early weapons development, and the use of tri-n-butyl phosphate (TBP) as an extractant for U and Pu (plutonium)
- In recent years, there has been a good deal of development of solvent extraction processes for the removal of the transuranic elements, ^{90}Sr , and ^{137}Cs from acidic high level waste.
- Laboratory demonstrations of the TRUEX process that uses the neutral extractant CMPO (octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide) to separate the transuranium elements from acidic high-level waste have been successful.
- More recently crown ethers have been used as specific extractants for Sr and Cs.

Ion Exchange

Ion exchange is one of the most popular radiochemical separation techniques due to its high selectivity and the ability to perform separations rapidly. In ion exchange, a solution containing the ions to be separated is brought into contact with a synthetic organic resin containing specific functional groups that selectively bind the ions in question. In a later step the ions of interest can be removed from the resin by elution with another suitable solution that differs from the initial solution. Typically the solution containing the ions is run through a column packed with resin beads. The resins are typically cross-linked polystyrenes with attached functional groups. Most cation exchangers (such as Dowex 50) contain free sulfonic acid groups, SO_3H , where the cation displaces the hydrogen ion. Anion exchangers (such as Dowex 1) contain quaternary amine groups, such as $\text{CH}_2\text{N}(\text{CH}_3)_3\text{Cl}$ where the anion replaces the chloride ion. The resin particles have diameters of 0.08 – 0.16 mm and exchange capacities of 3--5 meq per gram of dry resin.

It is common to absorb a group of ions on the column material and then selectively elute them. Complexing agents, which form complexes of varying solubility with the absorbed ions, are used as eluants. A competition between the complexing agent and the resin for each ion occurs and each ion will be exchanged between the resin and the complexing agent several times as it moves down the column.

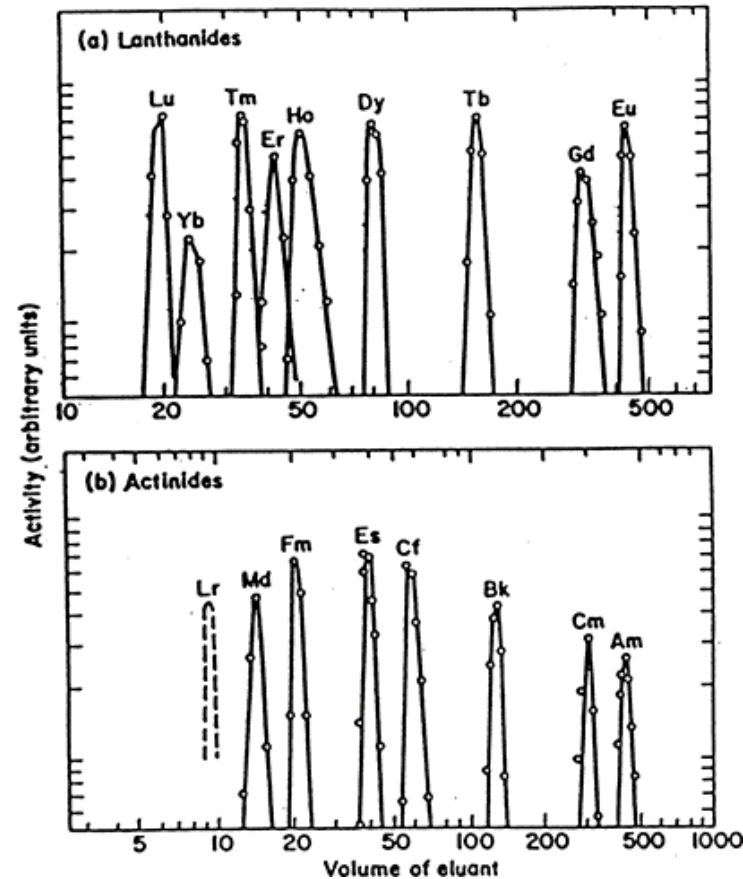


Fig. Elution of tri positive lanthanide and actinide ions on Dowex--50

In solvent extraction, the species to be separated is transferred between two immiscible or partially miscible phases, such as water and a nonpolar organic phase. To achieve sufficient solubility in the organic phase, the species must be in the form of a neutral, non-hydrated species. The transfer between phases is achieved by selectively complexing the species of interest causing its solubility in water to decrease with a concomitant increase in its solubility in the organic phase.

A hydrated metal ion (M^{Z+}) will always prefer the aqueous phase to the organic phase.

To get the metal ion to extract, some or all of the inner hydration sphere must be removed.

The resulting complex must be electrically neutral and organophilic, that is, have an

organic "surface" that interacts with the organic solvent. This can be done by:

- a forming a neutral complex MA_Z by coordination with organic anions A^-
- b replacing water in the inner coordination sphere by large organic molecules B such that one forms MB_N^{Z+} which is extracted into the organic phase as an ion-association complex $(MB_N)^{Z+} L_x^{Z-}$
- c forming metal complexes of form ML_N^{Z+N} with ligands (L) such that they combine with large organic cations RB^+ to form ion pair complexes $(RB^+)_N (ML_N)^{N+Z}$

Example:

An example is the extraction of uranyl nitrate.

In presence of additional nitrate, the increase in the concentration of the nitrate ion in the aqueous solution shifts the equilibrium between uranyl ion and nitrate complex towards the formation of latter, which facilitates a more complete extraction of the uranium into the organic solvent.

Salting out effect (salt-induced precipitation): Salting out agent has more affinity towards water, it becomes hydrated by the water molecules so that the substance to be extracted is really dissolved in a smaller amount of water, as a result the distribution coefficient between the aq and org phase is increased

Salting in refers to the effect where increasing the ionic strength of a solution increases the solubility of a solute, such as a protein

The solubility of proteins usually increases slightly in the presence of salt, referred to as "salting in". However, at high concentrations of salt, the solubility of the proteins drop sharply and proteins can precipitate out, referred to as "salting out".

The addition of salt increases the surface tension of the droplets and increases the density of the aqueous layer, thereby forcing separation. If one of the solvents being used is water, the addition of a saturated aqueous sodium chloride solution will help destroy the emulsion.

Salting-out Liquid-Liquid Extraction (SALLE)

It has long been known that the addition of an inorganic salt into a mixture of water and a water-miscible organic solvent causes a separation of the solvent from the mixture and the formation of a two-phase system . Sometimes this phenomenon is referred to as "salt-induced phase separation." Observations of this "salting-out" phenomenon were made for a number of water-miscible organics such as acetone, methanol, ethanol, and acetonitrile. Different salts and different salt concentrations will cause different degrees of phase separation. The high-polarity, water-miscible solvents used in salting-out systems have been investigated for extraction or concentration of many analytes that cannot be extracted by conventional LLE methods. This salting out often occurs at high salt concentrations. In some cases, the "salting-out" (or perhaps better termed "sugaring out") effect also can be achieved with high concentrations of saccharides .

Advantages of Liquid-liquid solvent extraction

1. Process can be continued with lesser amount of solute. It can be applied to a wide range of concentration
2. 2. wide scope of application
3. It can be performed with simple equipment, but can also automated

Disadvantages of Liquid-liquid solvent extraction

1. Often requires toxic or flammable solvents
2. Can be time consuming, especially if attainment of equilibrium is slow
3. Can require costly amounts of organic solvents and generate large volumes of organic waste
4. Can be affected by small impurities in the solvents
5. Multiple extraction might be required, thereby increasing time, consumption of materials and generation of waste
6. Tracer levels of analytes can form radiocolloids that can not be extracted, dissociate into less soluble forms or adsorb on the container surface or onto impurities in the system

Advantages of Solid-phase extraction method

1. Column/filter extraction is very selective
2. Generates a low volume of waste, can often be applied to samples dissolved in very acidic media
3. Requires relatively inexpensive equipment

Disadvantages of Solid-phase extraction method

1. Extraction columns can not be reused-a cost factor
2. Flow rate through columns are generally slow (1-3 mL/min)